

AFOSR FINAL REPORT

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Research Title: Metallo-Carbohedrenes - - Study of a New Class of Materials and Some Other Related Transition Metal Nitrides and Silicides

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I. Introduction

Clusters comprised of transition metal compounds of carbon, nitrogen and silicon form the basis of potentially important new ceramic-like and semiconductor materials that are expected to have novel electronic and optical properties, and perhaps may find use as light-weight construction and corrosion resistant materials as well. Several years ago we discovered an especially interesting new class of cluster materials referred to as metallocarbohedrenes, or Met-Cars for short, and we are actively pursuing investigations of their mechanisms of formation and production through an existing AFOSR grant.

This AASERT proposal supported two U.S. citizens who were interested in conducting their Ph.D. research in the newly emerging field dealing with the chemical physics of materials. This experience will place the students at the cutting edge of research in the general area of molecular dynamics, and trained them in advanced laser and high-tech instrumentation techniques. Their addition to the program enabled us to undertake a wider range of investigations into the unique properties of Met-Cars and related species, which provided results of direct value to the U.S. Department of Defense. Moreover, in the long term the training of young scientists in this emerging is of value to the DOD and the nation at large, enabling them to pursue careers in areas critical to maintaining our preeminence in the science and technology of advanced materials, and in chemical physics research. The specific areas in which these two students were involved comprised detailed investigations of the dynamics of ionization of various clustered materials, containing Met-Cars. These results yielded new insights into the properties of these and related cluster systems, and also provided new information for assessing the various theoretical calculations being made of cluster structures and properties.

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II. Brief Overview of our Laboratory Studies Focused on Laying the Foundation for Producing New Classes of Materials: Metallo-Carbohedrenes and Related Transition Metal Nitrides and Silicides

Since the inception of this AFOSR-sponsored program, we have made great strides in developing an understanding of the mechanisms of formation of Met-Cars, discovered several years ago in our laboratory, and also elucidating some of their unique characteristics. We endeavor to expeditiously publish our findings as soon as they become available, and the details of many of our accomplishments during the last several years are now available in the open scientific literature. Progress reports for the ASSERT Grant, as well as the prior AFOSR Grant entitled "Metallo-Carbohedrenes: Study of a New Class of Materials and Some Other Related Transition Metal Nitrides and Silicides," have been provided, and other details were given in the renewal grant application "Clusters of Transition Metal Compounds: Building Blocks of New Materials" which commenced April 1, 1997.

Very briefly, some of our most significant findings sponsored by the AFOSR are as follows:

- Extensive studies were conducted of the metastable dissociation of binary metal Met-Cars which provided confirming evidence in the case of the binary systems, of the important role of carbon loss at the point of cage closing. This strongly supports the mechanism of Met-Car formation as involving the statistical assembly of MC_2 units until the point of cage closure, whereupon two C_2 units are lost.
- Photoaction/photodissociation spectroscopy was employed to investigate the photophysics of binary metal Met-Cars. A new technique involving energy analysis of the products was developed which leads to a very accurate way of identifying the products of the dissociation. Detailed experiments were conducted for Ti_7YC_{12} , Ti_7ZrC_{12} and Ti_7NbC_{12} , among a wide variety of other species. The first in this series has one less electron than the Ti_7ZrC_{12} which is isoelectronic with Ti_8C_{12} . One theory predicted that electron deficient Met-Cars might be destabilized. On the other hand, Ti_7NbC_{12} has one more electron which is thought to play a role in enhancing the stability. Our experiments reveal that there is no discernible difference in the metal loss for any of these species, showing only a Ti loss for the dissociation pathway and no indication of a loss of a substituted metal for any stages of the photodissociation investigated.
- The ionization potentials of pure Ti and pure Zr Met-Cars were investigated using a technique rather different from the one employed by the Duncan group. In contrast to their results, the value deduced from our measurements agrees very well with literature values based on theoretical calculations employing the density functional approach. The key in deducing accurate ionization potentials was found to involve the production of fully dehydrogenated Met-Car building blocks.
- Investigations of the electron excitation and relaxation dynamics of Met-Cars were conducted using ultrafast laser pump-probe techniques. New information about the process of ionization was obtained, showing that the lifetimes of the excited intermediate state were less than 200 fs. Theoretical computations of the electronic states involved are currently in progress.

- A covariance technique was implemented for solving the nagging problem of cluster fragmentation which plagues identification of cluster parentages in many experiments. We first successfully applied this new technique to investigations of multicharged species originating from the high intensity laser irradiation of ammonia clusters. Thereafter, in preliminary investigations we have shown that this method is applicable to the study of Met-Cars, and we have employed it to show that the doubly charged metal atom emissions upon photoexcitation originate from the Met-Car species.
- A new apparatus was completed for use in a laser vaporization technique which we are employing to produce and collect bulk quantities of Met-Car soot. It enables direct laser desorption time-of-flight mass spectrometry without exposing the samples to air. We have found that this new laser vaporization production technique enhances the yield of Met-Cars in the soot.
- UV-Visible spectra reveal an interesting peak in several solvents employed to extract Met-Cars from soot. The peaks are centered in the region of 704 nm. In addition, very encouraging Raman spectral data has been obtained in recent experiments, and we are currently analyzing these data and trying to ascertain the extent of Met-Car separations attributable to purification versus carryover due to entrainment of fine particles.
- A series of experiments were conducted to ascertain the equivalence of the eight metal sites in the Met-Car. Questions had arisen with regard to earlier experiments utilizing small polar molecules as titrants; in the most recent work, butanol was also found to coordinate to each of the eight sites without any impediment due to steric hindrance. Our results are compatible with some observations of non-polar molecules binding to Met-Cars which display differences for the first four attachments. This is in accord with a model of π -bonding adsorption phenomena similar to that which is observed for aromatic molecules on metal surfaces.
- Extensive investigations have been conducted of the formation of binary metal Met-Cars. It had been predicted that $\text{Ti}_4\text{Zr}_4\text{C}_{12}$ might display a preferentially stable species if the double capped tetrahedron model for Met-Cars was the actual structure. All of our experiments show that the substitution of zirconium into the titanium Met-Car follows a statistical pattern with no site preference indicated.
- An extensive investigation of the delayed ionization mechanism which we discovered in Met-Cars, has been made for species having a variety of binary metal compositions. We have found that the phenomena appears over a wide range of the spectral region, indicating that all of phase space is being sampled and that triplet states are evidently not involved in the observed delayed ionization phenomenon. The data show a non-monotonic behavior with respect to metal substitution which is found to correlate very well with the ionization potential/work functions. Our data have now been fit to analytical expressions available from the Klotz' theory. All of this points to the phenomenon being a microscopic manifestation of thermionic emission which is observed for bulk metals having high cohesive energies.

IIIa. List of Publication Sponsored by AFOSR Since This Grant Commenced April 30, 1998.

- [‡]407. "Met-Cars: A New Family of Metal-Carbon Clusters," A. W. Castleman, Jr., in *Applications of Organometallic Chemistry in the Preparation and Processing of Advanced Materials* (J. F. Harrod and R. M. Laine, Eds.) NATO ASI Series E: Appl. Sci., Vol. 297, Kluwer Academic Publishers, The Netherlands, pp 269-281 (1995).
- [‡]415. "Delayed Ionization and Delayed Atomic Ion Emission of Ti and V Metallocarbohedrenes: Evidence for Collective Electronic Effects," B. D. May, S. F. Cartier and A. W. Castleman, Jr., *Chem. Phys. Lett.* **242**, 265-272 (1995).
- [‡]417. "Studies of Met-Car Adducts: $Ti_8C_{12}^+(M)_n$ (M=halogens, π -bonding molecules and polar molecules), H. T. Deng, K. P. Kerns, and A. W. Castleman, Jr., *J. Am. Chem. Soc.* **118**, 446-450 (1996).
- [‡]418. "Dynamics of Cluster Reactions and Ionization: From Semiconductor to Hydrogen-Bonded/van der Waals Systems," A. W. Castleman, Jr., B. D. May, S. F. Cartier, K. P. Kerns, H. T. Deng, E. M. Snyder, and S. A. Buzza, *NATO ASI Series on Large Clusters of Atoms and Molecules*, Kluwer Academic, Dordrecht, pp 371-404 (1996).
- [‡]*429. "The Delayed Ionization and Atomic Ion Emission of Binary Metal Metallocarbohedrenes $Ti_xM_yC_{12}$ (M = Zr, Nb; $0 \leq y \leq 4$; $x + y = 8$)," S. F.

- Cartier, B. D. May and A. W. Castleman, Jr., *J. Chem. Phys.* **104**, 3423-3432 (1996).
- †*433. "On the Formation, Structure and Stabilities of Metallocarbohedrenes," S. F. Cartier, B. D. May and A. W. Castleman, Jr., *J. Phys. Chem.* **100**, 8175-8179 (1996).
- †434. "Collision Induced Dissociation of Vanadium-Carbon Cluster Cations," K. P. Kerns, B. C. Guo, H. T. Deng and A. W. Castleman, Jr., *J. Phys. Chem.* **100**, 16817-16821 (1996).
- †435. "Delayed Ionization of and Delayed Atomic Emission from Metallocarbohedrenes," B. D. May, S. F. Cartier, and A. W. Castleman, Jr., in *Science and Technology of Atomically Engineered Materials* (P. Jena, S. N. Khanna, B. K. Rao, Eds.) World Scientific, Singapore, pp 207-214 (1996).
- †*438. "Clusters: Structure, Energetics, and Dynamics of Intermediate States of Matter," A. W. Castleman, Jr. and K. H. Bowen, Jr., Centennial Issue of *J. Phys. Chem.* **100**, 12911-12944 (1996).
- †440. "The Influence of Solvation on Ion-Molecule Reactions," A. W. Castleman, Jr., in *Advances in Gas Phase Ion Chemistry* (L. M. Babcock and N. G. Adams, Eds.) JAI Press, Connecticut, **3**, 185-253 (1998).
- †444. "Clusters in Intense Laser Fields: Multiple Ionization and Coulomb Explosion," E. M. Snyder, D. A. Card, D. E. Folmer and A. W. Castleman, Jr., in *Resonant Ionization Spectroscopy 1996*, (N. Winograd and J. Parks, Eds.), Institute of Physics Series, AIP Press, 379-382 (1997).

- ‡*446. "Photodissociation of Binary Metal Metallo-carbohedrenes," B. D. May, S. E. Kooi, B. J. Toleno and A. W. Castleman, Jr., *J. Chem. Phys.* **106**, 2231-2238 (1997).
- ‡451. "Covariance Mapping of Ammonia Clusters: Evidence of the Connectiveness of Clusters with Coulombic Explosion," D. A. Card, D. E. Folmer, S. Sato, S. A. Buzza, and A. W. Castleman, Jr., *J. Phys. Chem.* **101**, 3417-3423 (1997).
- ‡453. "Titanium-Carbon Clusters: New Evidence for High Stability of Neutral Met-Cars," H. Sakurai and A. W. Castleman, Jr., *J. Phys. Chem.*, **101**, 7695-7698 (1997).
- ‡*454. "Metallo-carbohedrenes: The Quest for New Materials," B. J. Toleno, H. Sakurai, S. E. Kooi, J. L. Baling, M. E. Lyn, and A. W. Castleman, Jr., *Proc. Ninth International Conference on High Temperature Materials Chemistry (HTMC IX)*, The Pennsylvania State University (K. E. Spear, Ed.), 637-647 (1997).
- ‡*460. "Delayed Ionization in Transition Metal-Carbon Clusters: Further Evidence for the Role of Thermionic Emission," S. E. Kooi and A. W. Castleman, Jr., *J. Chem. Phys.* **108**, 8864-8869 (1998).
- *461. "Molecular Dynamics Simulation of Coulomb Explosion Processes," L. Poth and A. W. Castleman, Jr., *J. Phys. Chem.* **102**, 4075-4081 (1998).
- *463. "Ionization Potentials for the Titanium, Zirconium, and Mixed Metal Met-Cars," H. Sakurai and A. W. Castleman, Jr., *J. Phys. Chem. A*, **102**, 10486-10492 (1998).

*465. "Arresting Intermediate States in a Chemical Reaction on a Femtosecond Time

Scale: Proton Transfer in Model Base Pairs," D. E. Folmer, L. Poth, E. S.

Wisniewski, and A. W. Castleman, Jr., *Chem. Phys. Lett.* **287**, 1-7 (1998).

*465. "Charge Stripping Effects from Highly Charged Iodine Ions Formed from

Coulomb Explosion of CH₃I Clusters," L. Poth, Q. Zhong, J. V. Ford, and A.

W. Castleman, Jr., *Chem. Phys.* **239**, 309-315 (1998).

‡*A. "Delayed Ionization in Binary Metal Met-Cars: The Role of Electronic States," S. E. Kooi and A. W. Castleman, Jr. (in preparation).

*B. "Ultrafast Excitation and Relaxation Dynamics of Met-Cars," S. F. Kooi, N. Kestner, and A. W. Castleman, Jr., (in preparation).

‡ AFOSR Grant F49620-97-1-0183

* AFOSR Grant F49620-95-1-0353

Iib. List of Seminars, Posters, Talks, During the Report Period May 1, 1995 – April 30, 1998 AFOSR Sponsored Research

"Dynamics of Ionization and Reactions in Molecular Clusters," The US/Japan Seminar on Dynamics, Photophysical and Photochemical Events Involving Clusters, Oahu, Hawaii, March 9-13, 1994.

"Femtosecond Reaction Dynamics of Ammonia Clusters," invited talk, American Chemical Society National Meeting, San Diego, CA, March 13-17, 1994.

"Met-Cars: Formation and Properties," invited talk, American Physical Society Meeting, Pittsburgh, PA, March 21-25, 1994.

"Reactions and Dissociation Dynamics of Met-Cars," (poster presented by K. P. Kerns and B. C. Guo), American Physical Society Meeting, Pittsburgh, PA, March 21-25, 1994.

"Growth of Metallo-Carbohedrenes: Face-Centered Cubic or Multicage Structures?" (poster presented by J. Purnell, S. A. Buzza and E. M. Snyder), American Physical Society Meeting, Pittsburgh, PA, March 21-25, 1994.

"Water Clusters: Contributions of Binding Energy and Entropy to Stability," (poster presented by Z. Shi and J. V. Ford), American Physical Society Meeting, Pittsburgh, PA, March 21-25, 1994.

"Production of Pure and Binary Metal Metallocarbohedrenes by the Direct Laser Vaporization of Carbides and Metal/Carbide Mixtures," (poster presented by S. F.

- Cartier and B. D. May), American Physical Society Meeting, Pittsburgh, PA, March 21-25, 1994.
- "Clusters: Getting the Magic Out of Magic Numbers," invited colloquium, Department of Physics and Astronomy, Rutgers University, Piscataway, NJ, April 6, 1994.
- "Clusters: A World of Cages," invited seminar, Department of Chemical Engineering, Rensselaer Polytechnic Institute, Troy, NY, April 13, 1994.
- "Met-Cars: Transition Metal-Carbon Molecular Clusters," invited talk, 185th Society Meeting of the Electrochemical Society on *Fullerenes: Physics, Chemistry, and New Directions VI* Symposium, San Francisco, CA, May 22-24, 1994
- "Metal Cluster Alloys and Oxides: Elucidating Structural and Electronic Effects in Governing the Reactivity and Catalytic Role of Matter in Finite Dimensions," invited talk, Ninth DOE/BES Heterogeneous Catalysis Surface Chemistry Meeting, Oconomowoc, WI, May 24-27, 1994.
- "Gas Phase Reactions of N_2O_5 with Protonated Water Clusters, $H^+(H_2O)_{n=3-30}$, and Hydrated Anions $X^-(H_2O)_{n \leq 5}$, $X=O, OH, O_2, HO_2$ and O_3 ," (presented by H. Wincel) Polish-Danish Symposium on Transient Ionic Species and Excited Molecules on Radiation Chemistry and Spectroscopy," Warsaw, Poland, June 4-7, 1994.
- "Clusters and the Solid State," invited talk, 8th International Congress of Quantum Chemistry, Prague, Czechoslovakia, June 19-23, 1994.
- "Metallo-carbohedrenes (Met-Cars) and Their Role in Reactions and Catalysis," invited talk, Quantum Chemical Aspects of Heterogeneous Catalysis, Berlin, Germany, June 26-28, 1994.
- "The Production and Properties of Met-Cars," invited talk, Eighth CIMTEC World Ceramics Congress, Florence, Italy, June 29-July 4, 1994.
- "Cluster Interests Related to Catalysis and New Electronic Materials," invited talk, University Research Initiatives on Clusters and Clusters Assemblies, Annapolis, MD, July 15, 1994.
- "Met-Cars: A Unique Class of Transition Metal-Carbon Molecular Clusters," invited talk, 1994 Gordon Research Conference on Inorganic Chemistry, Wolfeboro, NH, July 31-August 5, 1994.
- "Formation and Metastable Decomposition of Unprotonated Ammonia Cluster Ions Upon Femtosecond Ionization," (presented by S. A. Buzza) American Chemical Society Meeting, Washington, DC, August 21-25, 1994.
- "The Production of Individual and Binary Metal Metallo-carbohedrenes by the Direct Laser Vaporization of Carbides or Metal/Carbide Mixtures," (presented by S. F. Cartier and B. D. May) American Chemical Society Meeting, Washington, DC, August 21-25, 1994.
- "Binary Element Metallo-carbohedrenes," (presented by H. T. Deng) American Chemical Society Meeting, Washington, DC, August 21-25, 1994.

- "Gas Phase Reactions of $X(H_2O)_n$, $X = O, OH, O_2, HO_2$ and O_3 , with N_2O_5 ," (presented by H. Wincel) International Mass Spectrometry Conference, Budapest, Hungary, August 29-September 2, 1994.
- "Met-Cars: A New Family of Metal-Carbon Clusters," invited talk, NATO ARW on Applications of Organometallic Chemistry in the Preparation and Processing of Advanced Materials," Cap d'Agde, France, September 5-9, 1994.
- "Met-Cars and TiO Clusters," invited talk, DuPont Research and Development Experimental Station, Wilmington, DE, September 20, 1994.
- "Formation and Metastable Decomposition of Unprotonated Ammonia Cluster Ions upon Femtosecond Ionization," (presented by S. A. Buzza), Tenth Interdisciplinary Laser Science Meeting, Dallas, TX, October 2-7, 1994.
- "Met-Cars: A Unique Class of Molecular Clusters," invited seminar, Department of Chemistry, University of California, San Diego, La Jolla, CA, October 11, 1994.
- "Met-Cars: A New Class of Molecular Clusters," invited colloquium, Department of Chemistry, University of Nebraska, Lincoln, NB, October 14, 1994.
- "Met-Cars: A Unique Class of Molecular Clusters," invited talk, Harvard/MIT Combined Physical Chemistry Series, Harvard/Massachusetts Institute of Technology, Cambridge, MA, October 21, 1994.
- "Metallocarbohedrenes: Study of a New Class of Materials and Some Other Related Transition Metal Nitrides and Silicides," 1994 Molecular Dynamics and Inorganic Materials Contractors' Conference, National Academy of Sciences, Washington, DC, October 23-26, 1994.
- "Met-Cars: A Unique Class of Materials," invited seminar, Department of Chemical Engineering, Pennsylvania State University, December 1, 1994.
- "Exciting Matter of Nanoscale Dimensions, 1. Clusters: A World of Cages, Magic Numbers, and Building Blocks of Condensed Matter; 2. Met-Cars: A Unique Class of Molecular Cluster Materials; 3. An Ultrafast Glimpse of Reactions in Clusters," invited Distinguished Lecture Series, *Frontiers in Chemical Research*, Texas A&M University, College Station, TX, December 5-7, 1994.
- "Clusters: The Fifth State of Matter," invited seminar, Department of Chemistry, Cleveland State University, January 13, 1995.
- "An Ultrafast Look at Cluster Reactions," invited seminar, Stanford University, Stanford, CA, April 10, 1995.
- "Shedding Light on Met-Cars -- A Unique Class of Molecular Clusters," invited seminar, University of California, Berkeley, CA, April 11-12, 1995.
- "Dynamics of Cluster Ionization Following Multiphoton Absorption of High Intensity Ultrafast Laser Pulses, invited talk, Yamada Conference XLIII on Structures of Clusters, Shimoda, Shizuoka, Japan, May 10-13, 1995.
- "Clusters: The Interplay Between Experiment and Theory," invited seminar, The University of Tokyo, Japan, May 15, 1995.

- "Met-Cars: A Unique Class of Molecular Clusters," invited seminar, The University of Tokyo, Japan, May 15, 1995.
- "Dynamics of Cluster Ionization Following Multiphoton Absorption of High Intensity Ultrafast Laser Pulses," invited talk, The XVI International Symposium on Molecular Beams, Ma'ale Hachamisha, Israel, May 21-26, 1995.
- "Shedding Light on Met-Cars: A New Class of Molecular Clusters," invited seminar, Göteborg University, Göteborg, Sweden, May 29, 1995.
- "Metal Carbon Clusters," invited talk, NATO Advanced Study Institute, Erice, Italy, June 20, 1995.
- "van der Waals and Hydrogen Bonded Cluster Reactions," invited talk, NATO Advanced Study Institute, Erice, Italy, June 29, 1995
- "Intracluster Excited State and Ion-Molecule Reaction Dynamics of Weakly Bound Clusters," invited talk, Femtochemistry: The Lausanne Conference, Lausanne, Switzerland, September 4-8, 1995.
- "Coulomb Explosion of Multicharged Clusters Produced in Intense Radiation Fields," invited talk, Optical Society of America Annual Meeting/ILS-XI Conference, Portland, Oregon, September 10-15, 1995.
- "The Properties and Reactions of Binary-Metal Met-Cars," invited talk, International Symposium on the Science and Technology of Atomically Engineered Materials, Richmond, VA, October 30-November 4, 1995.
- "Delayed Ionization of and Delayed Atomic Ion Emission from Metallo-carbohedrenes," (poster presented by Brent D. May), International Symposium on the Science and Technology of Atomically Engineered Materials, Richmond, VA, October 30-November 4, 1995.
- "Observation of Atomic-Like Resonance in Multiphoton Ionization Spectrum of $(\text{CaO})_n\text{Ca}$ Clusters," (poster presented by Dr. Martin Foltin), International Symposium on the Science and Technology of Atomically Engineered Materials, Richmond, VA, October 30-November 4, 1995.
- "Delayed Ionization and Delayed Atomic Emission from Met-Cars," poster, 1995 International Chemical Congress of Pacific Basin Societies, Honolulu, HI, December 17-22, 1995.
- "The Ionization and Reaction Dynamics of Met-Cars," invited talk, 1996 Sanibel Conference on "Metal-Containing Ions and Their Applications in Mass Spectrometry," Tampa, FL, January 20-23, 1996.
- "Shedding a Little Light on Clusters," invited Chemical Physics Seminar, California Institute of Technology, Pasadena, CA, February 20, 1996.
- "Delayed Ionization of and Delayed Atomic Emission from Metallo-carbohedrenes," poster, 1996 March Meeting of the American Physical Society, St. Louis, MO, March 18-22, 1996.

- "Novel Mass Spectrometric Probes of Cluster Dynamics," invited talk, American Chemical Society Meeting, New Orleans, LA, March 25-29, 1996.
- "Delayed Ionization of and Delayed Atomic Emission from Metallocarbohedrenes," invited talk, 70th Colloid and Surface Science Symposium, Clarkson University, June 16-19, 1996.
- "Cluster Reactions: An Approach to Understanding the Fundamentals of Heterogeneous Catalysis," poster, Tenth DOE/BES Heterogeneous Catalysis and Surface Chemistry Conference, Montgomery, TX, May 21-24, 1996.
- "Met-Cars: Optical Excitation and Dynamics of Ionization," invited talk, 1996 Molecular Dynamics Contractors Meeting, University of Colorado at Boulder, June 2-5, 1996.
- "Coulomb Explosion of Multicharged Clusters Produced in Intense Radiation Fields," keynote talk, Eighth International Symposium on Resonance Ionization Spectroscopy and Its Application, The Pennsylvania State University, June 30-July 5, 1996.
- "Metallocarbohedrene Ionization Dynamics: A Molecular Example of Thermionic Emission," (poster presented by Steven E. Kooi and Brian J. Toleno), Eighth International Symposium on Resonance Ionization Spectroscopy and Its Application, The Pennsylvania State University, June 30-July 5, 1996.
- "Clusters In Intense Laser Fields: Multiple Ionization and Coulomb Explosion," (poster presented by E. M. Snyder), Eighth International Symposium on Resonance Ionization Spectroscopy and Its Application, The Pennsylvania State University, June 30-July 5, 1996.
- "The Metastable Decay of Alkene Clusters After Photoionization," (poster presented by L. Poth and Q. Zhong), Eighth International Symposium on Resonance Ionization Spectroscopy and Its Application, The Pennsylvania State University, June 30-July 5, 1996.
- "Observation of Atomic-Like Resonance in Multiphoton Ionization Spectra of the Metal-Rich Magnesium-Oxide, Calcium-Oxide and Barium-Oxide Clusters," (poster presented by M. Foltin), Eighth International Symposium on Resonance Ionization Spectroscopy and Its Application, The Pennsylvania State University, June 30-July 5, 1996.
- "Delayed Ionization of and Delayed Atomic Emission from Metallocarbohedrenes," poster, Eighth International Symposium on Small Particles and Inorganic Clusters, Copenhagen, Denmark, July 1-6, 1996.
- "Dynamics of Intra-Cluster Reactions via Ultrafast Time-Resolved Spectroscopy," Opening Plenary Lecture, 14th International Symposium on Gas Kinetics, Leeds, United Kingdom, September 7-12, 1996.
- "Studies of Transition Metal Oxide Clusters: Gaining Insight into the Mechanisms of Catalysis," invited talk, DuPont Central Research & Development, Wilmington, DE, September 25, 1996.

- "Delayed Ionization of and Delayed Atomic Emission from Metallocarbohedrenes," invited talk, Fifth Annual Workshop of the Consortium for Nanostructured Materials, Nashville, TN, October 18-19, 1996.
- "Cluster Dynamics: From the Ultraslow to the Ultrafast," invited colloquium, Temple University, Philadelphia, PA, October 24, 1996.
- "Cluster Dynamics: From the Ultraslow to the Ultrafast," invited seminar, Max-Planck-Institut für Quanten-optik, Garching, Germany, November 1, 1996.
- "Dynamics of Ion Molecule Reactions in Clusters," invited poster presentation, 1997 Winter Gordon Research Conference on Structures, Energetics and Reaction Dynamics of Gaseous Ions; Discussion Leader for the Session on *Molecular Clusters*, Ventura, CA, February 23-27, 1997.
- "Met-Cars: A Unique Class of Molecular Clusters," invited colloquium, Department of Chemistry, University of California, Irvine, February 28, 1997
- "Met-Car Dynamics: Formation, Ionization and Dissociation," invited talk, 1997 American Physical Society March Meeting, Kansas City, MO, March 17-21, 1997.
- "Production and Analysis of Metallocarbohedrene Containing Soot," (presented by B. J. Toleno), 1997 American Physical Society March Meeting, Kansas City, MO, March 17-21, 1997.
- "Metal-Carbon Clusters: New Evidence for High Stability of Neutral Metallocarbohedrenes," (presented by H. Sakurai), 1997 American Physical Society March Meeting, Kansas City, MO, March 17-21, 1997.
- "Delayed Ionization in Transition Metal Carbon Clusters," (presented by S. E. Kooi), 1997 American Physical Society March Meeting, Kansas City, MO, March 17-21, 1997.
- "Dynamical Events in Clusters: From the Ultraslow to the Ultrafast," invited seminar, Princeton University, Princeton, NJ, April 3 1997.
- "Clusters: A Look at Intermediate States of Matter," invited lecture, The Joe L. Franklin Memorial Lecture, Rice University, Houston, TX, April 9, 1997.
- "Cluster Excitation and Ionization: From the Ultraslow to the Ultrafast," invited speaker, Special Sesqui-centennial Event at the City College of New York, Symposium on Molecular Aggregates: Photochemistry, Photophysics, Spectroscopy and Nonlinear Optics, New York, NY, April 11, 1997.
- "Molecular Clusters," invited speaker, Department of Energy Workshop, *From Molecules to Materials*, sponsored by the Division of Chemical Sciences, Austin, TX, April 30-May 2, 1997.
- "Met-Car and Metal Clusters: The Quest for New Materials," invited talk, Ninth International Conference on High Temperature Materials Chemistry (HTMC-IX), The Pennsylvania State University, University Park, PA, May 19-23, 1997.
- "Production and Analysis of Metallocarbohedrene Containing Soot," (poster presented by B. J. Toleno and J. L. Baling) Ninth International Conference on High Temperature

Materials Chemistry (HTMC-IX), The Pennsylvania State University, University Park, PA, May 19-23, 1997.

"Delayed Ionization in Transition Metal Carbon Clusters," (poster presented by S. E. Kooi) Ninth International Conference on High Temperature Materials Chemistry (HTMC-IX), The Pennsylvania State University, University Park, PA, May 19-23, 1997.

"Metal-Carbon Clusters: New Evidence for High Stability of Neutral Metallo-carbohedrenes," (poster presented by H. Sakurai) Ninth International Conference on High Temperature Materials Chemistry (HTMC-IX), The Pennsylvania State University, University Park, PA, May 19-23, 1997.

"Nickel Oxide Cluster Reactions with Nitric Oxide," (poster presented by W. D. Vann) Ninth International Conference on High Temperature Materials Chemistry (HTMC-IX), The Pennsylvania State University, University Park, PA, May 19-23, 1997.

"Bimetallic Clusters: Insights into Reactions of Subnanoscale Surfaces," (poster presented by R. L. Wagner) Ninth International Conference on High Temperature Materials Chemistry (HTMC-IX), The Pennsylvania State University, University Park, PA, May 19-23, 1997.

"Met-Cars: A New Class of Molecular Clusters," invited lecture, Institute for Molecular Science, Okazaki, Japan, May 26, 1997.

"Reaction Dynamics in Clusters: From the Ultraslow to the Ultrafast," invited plenary lecture, 13th Symposium on Chemical Kinetics and Dynamics, Japan Advanced Institute for Science and Technology, Kanazawa, Japan, May 29, 1997

"Dynamics of Intra-Cluster Reactions via Ultrafast Time-Resolved Spectroscopy," invited lecture, University of Kyushu, Fukuoka, Japan, June 2, 1997.

"Dynamics of Intra-Cluster Reactions via Ultrafast Time-Resolved Spectroscopy," invited lecture, Tohoku University, Sendai, Japan June 5, 1997.

"Opportunities in Cluster Research: An Overview of Cluster Research at Penn State," invited lecture, Genesis Institute, Toyoto Institute of Technology, Tokyo, Japan, June 7, 1997.

"NO_x Reactions with Nickel and Nickel Oxide Clusters: Elucidating Mechanisms Pertaining to Heterogeneous Catalysis," (talk given by W. D. Vann), 71st Colloid and Surface Science Symposium, University of Delaware, Newark, DE, June 29-July 2, 1997.

"Reactivities and Collision Induced Dissociation of Vanadium Oxide Cluster Cations," (talk given by R. C. Bell) 71st Colloid and Surface Science Symposium, University of Delaware, Newark, DE, June 29-July 2, 1997.

"Bimetallic Clusters: Insights into Reactions of Subnanoscale Surfaces," (talk given by R. L. Wagner) 71st Colloid and Surface Science Symposium, University of Delaware, Newark, DE, June 29-July 2, 1997.

- "Atmospheric Studies Using Cluster Ions: An Investigation into the Reactivity of Iodine Ion Species," (poster presented by R. S. MacTaylor) Fourth International Conference on Chemical Kinetics, National Institute of Standards and Technology, Gaithersburg, MD, July 14-18, 1997.
- "Photodissociation Dynamics of Methyl Iodide Clusters," (talk presented by L. Poth) Fourth International Conference on Chemical Kinetics, National Institute of Standards and Technology, Gaithersburg, MD, July 14-18, 1997.
- "Dissociation Dynamics of Hydrochloride Dimer Radical Cation," (poster presented by Q. Zhong) Fourth International Conference on Chemical Kinetics, National Institute of Standards and Technology, Gaithersburg, MD, July 14-18, 1997.
- "Analysis of Metallo-carbohedrene Containing Soot," (poster presented by B. J. Toleno) Twenty-Third Biennial Conference on Carbon, The Pennsylvania State University, July 13-18, 1997.
- "Delayed Ionization in Transition Metal-Carbon Clusters," (poster presented by S. E. Kooi) Twenty-Third Biennial Conference on Carbon, The Pennsylvania State University, July 13-18, 1997.
- "Metal-Carbon Clusters: New Evidence for High Stability of Neutral Metallo-carbohedrenes," (talk presented by H. Sakurai) Twenty-Third Biennial Conference on Carbon, The Pennsylvania State University, July 13-18, 1997.
- "Dynamics of Cluster Ionization: From the Ultraslow to the Ultrafast," invited seminar, Physics Department, University of Würzburg, Germany, July 18, 1997.
- "Structure and Reactions of Vanadium Oxide Clusters," (talk presented by K. Zemski) DuPont Experimental Station, Wilmington, DE, July 31, 1997.
- "Comparison of Vanadium, Niobium and Tantalum Oxide Clusters and Future Directions," (talk presented by R. Bell) DuPont Experimental Station, Wilmington, DE, July 31, 1997.
- "Clusters: Elucidating the Influence of Solvation on Reaction and Ionization Dynamics," invited lecture, Femtochemistry '97 Conference, Lund, Sweden, August 31-September 4, 1997.
- "Cluster Dynamics: From the Ultraslow to the Ultrafast," invited seminar, Physics/Chemistry Department, Chalmers University, Göteborg University, Sweden, September 5, 1997.
- "Exploring Cluster Dynamics in the Ultrafast Time Regime," 214th ACS National Meeting, Las Vegas, Nevada, September 7-11, 1997.
- "Clusters: Probing the Properties and Dynamics of Intermediate States of Matter," Opening Plenary Address in Celebration of the Millennium of Gdansk, Gdansk, Poland, September 19-22, 1997.
- "Elucidating Dynamical Events in Clusters Using Ultrafast Lasers," invited seminar, The Polish Academy of Science, September 29, 1997.

"Exploring Cluster Dynamics in the Ultrafast Time Regime," invited speaker, 13th Interdisciplinary Laser Science Conference: Symposium on Laser-Induced Chemistry in Clusters, Long Beach, CA, October 17-23, 1997.

"Shedding Some Light on Clusters," invited seminar, Department of Chemistry, Indiana University, Bloomington, IN, November 6, 1997.

"An Ultrafast Look at Reactions in Clusters," Gordon Research *Conference* on Molecular and Ionic Clusters, Ventura, CA, January 4-8, 1998.

"Production and Analysis of Metallocarbohedrene Containing Soot," (poster presented by Brian J. Toleno), 215th National Meeting of the American Chemical Society, Dallas, TX, March 23-April 2, 1998.

"Shedding Some Light on Met-Cars: A Unique Class of Molecular Clusters," invited colloquium, Department of Chemistry, Louisiana State University, Baton Rouge, LA, March 20, 1998.

"Shedding Some Light on Met-Cars: Prospective Building Blocks of New Materials," invited seminar, Physics Department, Virginia Commonwealth University, Richmond, VA, April 2, 1998.

"Shedding Some Light on Met-Cars: A Unique Class of Molecular Clusters," invited colloquium, Department of Chemistry, Johns Hopkins University, Baltimore, MD, April 21, 1998.

"Clusters: Prospects of Building Blocks for New Materials," invited colloquium, Department of Chemistry, University of Rochester, Rochester, NY, April 29, 1998.